

Viscosity Reduction in Extra Heavy Crude Oils

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Introduction

The next few years will see a change in the sources of crude oil in the global market. Advances in exploration and production technologies in the petroleum industry are creating new major sources in areas that were previously off limits for reasons of geography, politics and technology. Some of the new areas at exploitation will have a major significance on the US markets, namely, Latin America, especially Venezuela, and Canadian heavy oil and synthetic crude oil projects (1).

Latin American sources are expected to increase production to around 4.2 million bbl/day by 2005. Of this 1 million bbl/day is expected to be extra-heavy Orinoco oil from Venezuela. It has been projected that imports to the US from Latin America will increase by around 2.7 million bbl/day during the same period. As well as this, a big increase in crude oil production will come heavy crude oil reserves in Western Canada. These reserves are intended to be produced a diluted heavy crudes and as synthetic oils, with varying degrees of upgrading. It is expected that by 2005 another 700,00 bbl/day will be coming from Canadian heavy oil fields. Most of this will end up in the US Mid-West Market. This supply will replace the US supplies at lighter crude.

With such increases of heavy crude oil sources making there way into the US market in the near future now seems a good time to exploit new avenues of research into the reduction at their viscosity. Some of these crude oils can have viscosities in excess of 15,000 centistokes at 100°F (2). In order for these crude oils to be transported via pipeline from the source, the viscosity must be lower than 150 centistokes at 100°F. The crude oils being very viscous on extraction have to go through some processing e.g. gas plasticization, thermal cracking or blending with lighter distillate fractions, to enable them to be transported by pipeline.

Taking blending for an example, typically the crude oils are blended with a kerosene distillate fraction. This process has its disadvantages. In some cases up to 30 wt.% of kerosene must be added to sufficiently reduce the viscosity, this uses up a great quantity of a valuable commercial product. Also the added kerosene must be processed again through the refinery along with heavy crude oil.

It is widely assumed that the asphaltene molecules in oils agglomerate to form micelle-like clusters. Interactions between these clusters contribute towards the viscosity of the oils. By breaking these agglomerates apart viscosity will be reduced. The kerosene used to cut the oils and reduce viscosity only does so by being an effective diluent. It does not break down the agglomerates by any significant amount. The following work is from a scoping study, the objective of which was to see whether the viscosity of extra heavy crude oils could be reduced by the addition of other chemical compounds and/or distillate fractions, which may break down the asphaltene agglomerates, and thus achieve greater viscosity reductions, when compared with kerosene. The intention is to then augment the better of these additive compounds with kerosene, thus initiating viscosity reduction for less volume of diluent.

In this period of initial investigation several dispersants with differing physical and chemical properties have been assessed for their effect on viscosity reduction. Figure 1 shows the chemical structure and the polarity of the compounds, in Debye units (DU). The compounds were chosen for their ring type structures. The presence of π electrons in the ring may play a role in the interaction between the compounds added and the π electrons in the polyaromatic systems of the asphaltene agglomerates. The compounds were kept to one ring to keep the size of the molecules small and allow for a greater diffusion through the crude oil matrix, and penetration into the asphaltene agglomerates.

Experimental

All of the compounds used in this study were purchased from the Aldrich Chemical company, except for the xylenes mix which came from Marathon Oil's Texas City refinery. The sample characteristics of the extra heavy crude oil are shown in Table 1.

The experiments were performed using 70ml tubing bomb reactors, into which was placed a known weight of extra heavy crude oil. To this 2.4, 4.8 or 8.3 wt.% of additive compound was added, the reactor was sealed and purged with nitrogen gas. The reactors were placed into a heated sandbath and shaken for 2 hours at 200 °C. The resulting mixtures were then removed from the reactors and stored in sealed containers under nitrogen.

The viscosity measurements were carried out using a Brookfield DV-III programmable viscometer, fitted with Thermosel system for viscosity measurements at elevated temperatures. The viscosities were measured at 140 °F. The measurements were taken when the sample was at equilibrium. That is at the point when increases in the shear rate (related to spindle rotation) resulted in no or little (<1%) change in the viscosity measured. In other words the mixture exhibited signs of a Newtonian fluid.

Table 1. Sample characteristics of the extra heavy crude oil used in this study.

SAMPLE CHARACTERISTICS	
Carbon	76.6%
Hydrogen	10.5%
Nitrogen	0.7%
Sulfur	-
Average Molecular Weight	548
Liquid Density (g/ml)	1.013
API Gravity	8
Boiling Point/Wt%	>200 °C/99.8%
Viscosity (cP@140 °F)	7800

Results and Discussion

Figure 2 shows the raw viscosity/dispersant data to date. In the plot it can be seen that the additive compounds used have a diverse effect on viscosity. The major general trend to note is that with the increasing polarity of the dispersant there is an increase in the measured viscosity. The higher the polarity of an additive compound the stronger the dipole-dipole interactions are between them (3,4). Therefore they can break down the asphaltene agglomerates, but still have an attractive binding force throughout the mixture which in turn binds the molecules together and hence increases viscosity. The viscosity reduction however may not just be related to the break down of the asphaltene agglomerates. A more simple answer may be related to Eyring's theory of liquid viscosity (5). Although we have not looked in depth into using Eyring's theory, a relationship between dilution effects and viscosity can be deduced from it. More accurate calculations must be conducted including the relative densities, heats of vaporization, molar volumes and molecular weight of the as received compounds and the mixtures. However these calculations do not take into account the full effect of the dipole interactions, which are significant.

These are not the only factors worth noting. Solubility of the dispersant in the heavy crude will play a major role in viscosity reduction. If partial solubility or phase separation is occurring, then a lower than expected viscosity measurement will be recorded. This is because when phase separation occurs then the more fluid phase, i.e. the additive compound, may tend to concentrate around the spindle of the viscometer, and thus lower apparent viscosity. This would then explain why the viscosity measurements seems to be low for acetophenone and cyclohexanone (see Figure 3). We know that the crude oil sample is soluble in toluene, xylenes and the N-methyl pyrrolidinone. The curve in the line is too low where the cyclohexanone and acetophenone are. It is not likely that viscosity would level off when using miscible additive compounds with polarities between 1 and 3 DU. Therefore, partial solubility must be the cause for the lower measurements. However, solubility experiments should be conducted to prove this hypothesis.

Assuming that the heavy crude oils are soluble in the dispersants, then molecular size of the additive compound may have an important role in viscosity reduction. Smaller molecules or molecules with the correct physical and chemical characteristics to fit into the gaps between the asphaltene agglomerates can reduce the viscosity to a greater extent. This is caused by deeper penetration, which induces greater break up of the asphaltene agglomerates.

One of the goals of this work is to determine whether an additive compound could be added to the kerosene diluent and enhance viscosity reduction. This theory assumes that the additive can break down the asphaltene agglomerates. For this to take effect only a small quantity of additive compound may be needed. For example, if 1 wt.% is sufficient to initiate the breakdown of the asphaltene agglomerates, then less kerosene would be needed to cut the viscosity to a level required for pipeline transportation.

Figure 4 shows a plot of log log viscosity against weight percent of additive compound in the crude oil. From this we took the y axis intercept for each additive compound and plotted it against its polarity. The resulting plot (Figure 5) was produced. From this we can assume that at low concentrations of additive compound in the crude oil, a compound with a polarity of around 0.6-0.7 Debye units and the right structural and chemical characteristics could lower viscosity more than other additive compounds, due to its greater dispersive qualities. This conclusion however needs verification through a detailed study of additive compounds with polarities in this area, as well as studies using mixtures of kerosene and additive compounds.

It can be seen from the data in Figure 2 that when toluene or xylenes mix is used then the measured viscosities are up to 50% lower than the equivalent weight percent for kerosene. In areas of heavy oil extraction where a supply of these lighter distillates is available, then using toluene or a xylenes mix from the BTX fraction may be a viable alternative to kerosene. Also a lower volume of distillate would be used. An extra advantage is that toluene and xylenes have a low enough boiling point that they could be removed, at nearly a 100% yield, from the crude oil prior to processing. By setting up a recycle stream costs of the operation would be lowered considerably. Plus if the feed for the recycle stream needs to be topped up, toluene and xylenes are made from the heavy crude oils during the refining process.

Conclusions

In this period of initial investigation it has been shown that the viscosity of extra heavy crude oils can be reduced to a greater extent using some additive compounds, when compared to using the conventional diluent kerosene. Interesting interactions, related to polarity, have been observed between the additive compounds and the crude oil matrix. There may be some scope to initiate a computer simulation of these interactions, as well as studying the mechanism through which asphaltene agglomerates are broken apart. Further work must include the study of additive compounds with polarities between 0.5 and 2.5 Debye units. Also reduction in the quantity of additive compound to 1 wt.% and lower must be studied, to evaluate whether there is still a linear relationship to the viscosity reduction at low concentrations.

References

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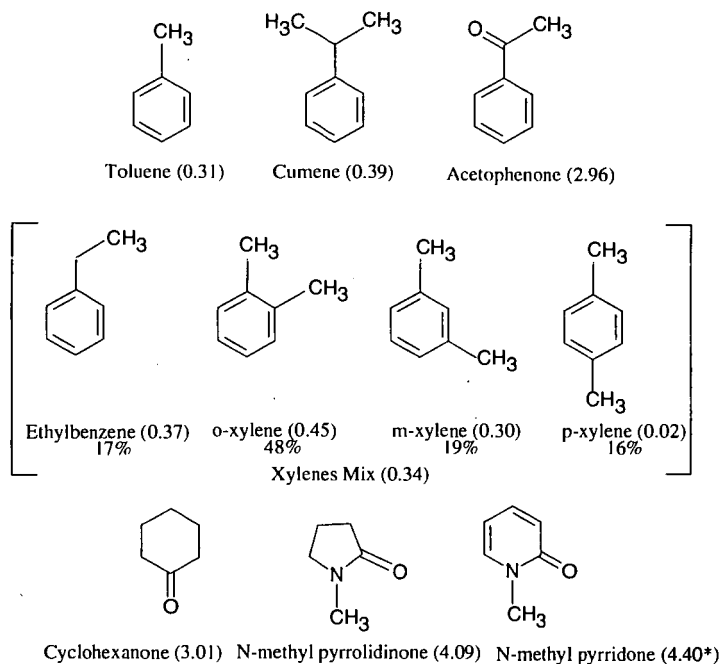


Figure 1. Chemical structures and polarities (in Debye units) of the additives used.

* This value was calculated. The rest were taken from known data (6).

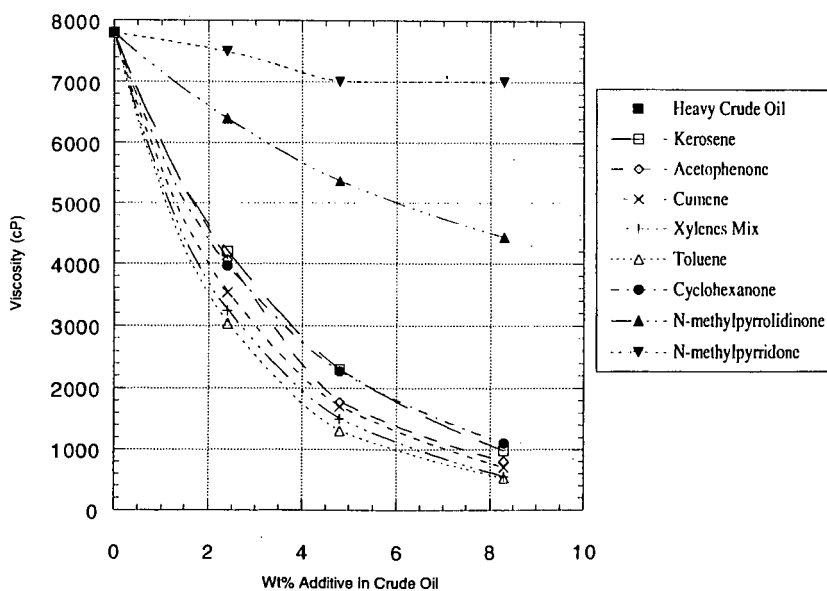


Figure 2. Plot of viscosity against wt.% of additive compound in the crude oil.

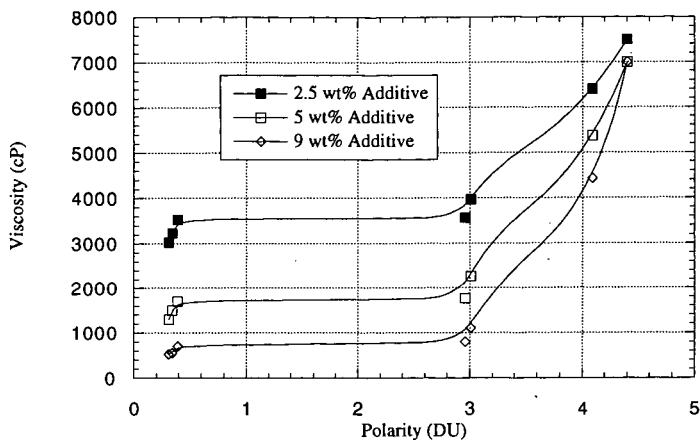


Figure 3. Plot of polarity of additives against measured viscosity

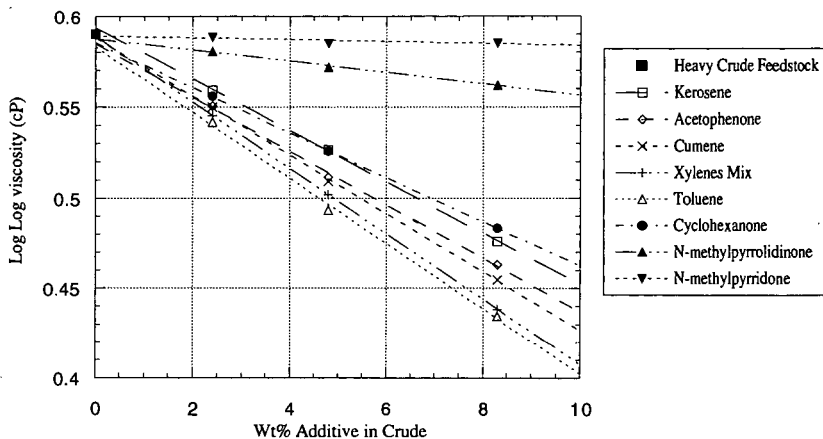


Figure 4. Log log viscosity vs. wt.% of additive in crude oil

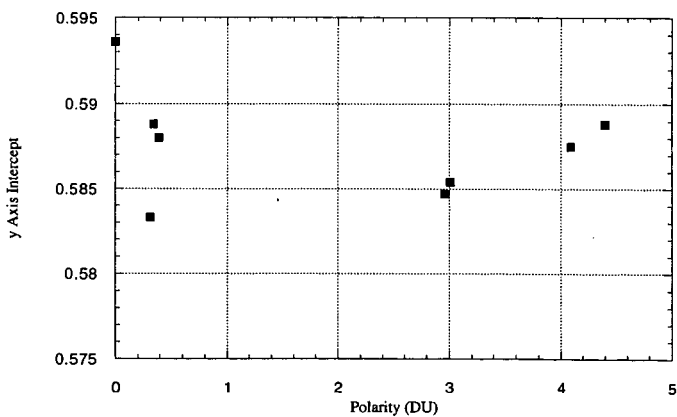


Figure 5. Plot of polarity of additive compounds against y axis intercepts from Figure 4.